

TERNARY AND QUATERNARY OXIDES OF Bi, Sr AND Cu

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Abstract. Among the phases present in the products of thermal treatments of mixtures of analytical grade Bi_2O_3 , $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and CuO , a cubic perovskite, $\text{BiSr}_3\text{O}_{5.5}$, with 1:1 order at the B-cations sublattice and $a = 8.493(7) \text{ \AA}$ has been found. This oxide appears to substitute some Cu for Bi giving rise to materials with lower a values. After been grown from mixtures of the same reagents at Bi:Sr:Cu molar ratios $(0.7-2.2):(1.0-2.2):1$ using techniques of static and revolving crucibles, crystals of four phases have been studied by X-ray diffraction, electron microscopy and electron diffraction, namely the superconducting Raveau oxide, A; a second phase, A_1 , very similar to A; and the oxides with Bi:Sr:Cu molar ratios 2:2:1, K; and 4:8:5, G. The conditions (composition, crystallization rate) which lead to A, A_1 or K are established. Each of these phases distinguishes from the two others by its oxygen content, which decreases in the order $A > A_1 > K$.

1. INTRODUCTION

Prior of the discovery¹ of superconductivity in an oxide of Bi, Sr and Cu, several solid phases were known in the two-component regions of the ternary system Bi_2O_3 - SrO - CuO . Nevertheless that discovery has created a new interest in ternary and quaternary copper oxides, of which the following phases are at present known.

Oxides of Bi and Cu. Although two compounds of stoichiometries Bi_4CuO_7 and $\text{Bi}_2\text{Cu}_2\text{O}_5$ have been mentioned^{2,3}, the oxide best characterized⁴⁻⁷ is tetragonal CuBi_2O_4 , with unit-cell parameters (\AA) $a = 8.510$, $c = 5.814$. The crystal structure of CuBi_2O_4 has been simultaneously refined^{6,7} in the space groups S.G. $P4/ncc$ (No. 130)⁸ and $I4$ (No. 79)⁹, with Cu in a square planar coordination.

Oxides of Sr and Cu. Whereas the existence of two Sr and Cu (II) oxides, Sr_2CuO_3 and SrCuO_2 , is well established, only the tetragonal oxide SrCu_2O_2 of Sr and Cu (I) is known¹⁰, with S.G. $I4_1/amd$ (No. 141)¹¹, $a = 5.48$, $c = 9.82$, SrO_6 octahedra and Cu in linear two-coordination with oxygen. Sr_2CuO_3 is^{12,13} orthorhombic, $a = 12.684$, $b = 3.9064$, $c = 3.4957$, S.G. $Immm$ (No. 71), and includes SrO_7 polyhedra and planar CuO_4 squares; and CuSrO_2 is^{3,14,15} also orthorhombic, $a = 3.9136(2)$, $b = 16.3313(8)$, $c = 3.5730(2)$, S.G. $Cmcm$ (No. 63). Besides a not too well characterized Sr cuprate (III) hydrate¹⁶, $\text{SrCu}_2\text{O}_4 \cdot n\text{H}_2\text{O}$, a new oxide of Sr and Cu containing some Cu (III) and formulated as $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, has been recently reported^{17,18}. The crystal structure of orthorhombic $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ is incommensurate and can be described¹⁷ as the result of two interpenetrating structures: one with Sr-(Cu_2O_3 sheets)-Sr layers in an orthorhombic cell with dimensions (\AA) of $a = 11.459(2)$, $b = 13.368(5)$, $c = 3.931(1)$, and a second structure with layers of (CuO_2 chains) in a cell having the mentioned a and b values but with $c = 2.749(1)$.

Oxides of Bi and Sr. The first phase described^{19,20} in the system Bi_2O_3 - SrO is a rhombohedral solid solution with the homogeneity range $s = 14-26$, being s the mol percent Sr/(Sr+Bi). This phase, S.G. $R\bar{3}m$ (No. 166), has a rhombohedral primitive unit-cell with $a = 9.6-9.8 \text{ \AA}$ and $\alpha = 23.8^\circ-23.4^\circ$, or a thrice primitive hexagonal cell with $a = 3.97 \text{ \AA}$, $c = 28.1-28.6 \text{ \AA}$. In this oxide, that can be formulated as

$\text{Bi}_{2-2x}\text{Sr}_x\text{O}_{3-2x}$ with $x = 2s/(100+s)$, the metal lattice always seems to remain complete, whereas there is a variable number of vacant positions of the oxygen lattice.

The effect of small SrO additions on the polymorphism of Bi_2O_3 was studied some years later by high temperature X-ray diffraction, and the tentative partial phase diagram in the temperature range 500–900 °C was proposed²¹. This diagram includes the above mentioned rhombohedral phase of variable composition and a solid solution of cubic symmetry. The system Bi_2O_3 –SrO has been studied some years ago²², in the temperature range 620 to 1000 °C by thermal and high-temperature X-ray diffraction analyses. Table I includes the composition, approximate stability regions, crystal system, and unit-cell parameters of the different phases that were found, comprising five solid solutions and three oxides of constant composition, two of which

Table I. Approximate stability regions, symmetry, and unit-cell parameters for oxides^a of compositions $\text{Bi}_{2-2x}\text{Sr}_x\text{O}_{3-2x}$, according to reference 22.

Oxide	x	T °/C	Symmetry	a/Å	b/Å	c/Å
α_1	0.01–0.12	730–820	C	5.67	–	–
β_1	0.20–0.40	700–900	R	4.0	–	28.7
β_2	0.18–0.43	620–700	R	3.97	–	28.2
Bi_2SrO_4	0.50	620–800	–	–	–	–
γ	0.58–0.64	820–940	T	13.239(2) ^b	–	4.257(1) ^b
γ'	0.58–0.62	900–930	C	4.41 ^c	–	–
$\text{Bi}_2\text{Sr}_2\text{O}_5$	0.67	650–950	O	14.293(2)	7.651(2)	6.172(1)
$\text{Bi}_2\text{Sr}_3\text{O}_6$	0.75	810–980	–	–	–	–

C: cubic T: tetragonal R: rhombohedral O: orthorhombic M: monoclinic
^a excluding four metastable solid solution obtained by annealing α_1 in different conditions
^b for $x = 0.615$: see ref. 23. ^c for $T = 950$ °C

have been characterized more recently: Bi_2SrO_4 is²⁴ monoclinic, S.G. C2/m (No. 12), with $a = 19.2882(16)$, $b = 4.3520(4)$, $c = 6.1015(5)$, $\beta = 94.839(7)^\circ$; and $\text{Bi}_2\text{Sr}_2\text{O}_5$ is²⁵ orthorhombic, S.G. Pmam (No. 51) with the crystallographic constants $a = 6.1713(6)$, $b = 14.3074(15)$, $c = 3.8262(4)$, closely related to those shown in Table I. Some months ago a new oxide of molar ratio Bi:Sr = 1:3 ($x = 0.857$) has been described²⁶ as crystallizing in the orthorhombic system with $a = 17.147$, $b = 16.758$, $c = 16.998$ Å.

Oxides of Bi, Sr and Cu. The first superconducting material in the system Bi–Sr–Cu–O was described by the group of Raveau¹ and formulated as $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{7+x}$, with an orthorhombic unit-cell of parameters (Å) $a = 5.32$, $b = 26.6$, $c = 48.8$ and a superconducting transition at 7 K, which was soon confirmed²⁷. In a preliminary publication²⁸ our group reported that mixtures of Bi_2O_3 , SrCO_3 and CuO in the molar ratios Bi:Sr:Cu = 2:2:2 lead to the oxide $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$, here designed as 221, mixed with small amounts of CuO ; and that all the reflexions of the X-ray diffraction patterns of the 221 oxide can be indexed in an orthorhombic unit-cell of parameters (Å) $a = 5.390(2)$, $b = 26.973(8)$, $c = 24.69(4)$. Subsequent diffraction studies (X-ray, electron, neutron) confirmed the composition 221 and propounded the substructures included in Table II.

The actual structure of 221 is a long-period modulated superstructure with different modes that can be observed by electron diffraction and high-resolution electron microscopy. The presence of superstructures was soon established²⁷ and corroborated later by various authors^{32,35,37,26}. Superstructures of the following types

have been described³⁵: base-centered monoclinic with parameters (Å) $a = 5.4$, $b = 27$, $c = 26.9$, $\alpha = 66.3^\circ$; monoclinic with $a = 5.1$, $b = 27$, $c = 12.6$, $\alpha = 77.6^\circ$; and base-centered orthorhombic with $a = 5.4$, $b = 22.6$, $c = 24.6$.

Table II. Crystal structures proposed for the superconducting oxide of approximate composition $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$

Symmetry	S.G.	a/Å	b/Å	c/Å	(°)	Z	Ref.
T	-	5.381(1)	-	24.65(1)	-	-	29
T	I4/mmm	3.8097(4)	-	24.607(3)	-	2	30
O	Amaa	5.392	5.394	24.537	-	4	31
O	-	10.8	53	24	-	-	32
T	I4/mmm	3.801(3)	-	24.61(9)	-	2	33
O	Amaa	5.362(3)	5.374(1)	24.622(6)	-	-	34
T	-	5.4	-	24.6	-	-	35
M	C2	26.856	5.380	26.908	113.55	4	36
M	-	5.4	26	28	116	-	37

T: tetragonal O: orthorhombic M: monoclinic

Preliminary studies of the authors showed that some other phases appear for compositions Bi, 1.5-2.2; Sr, 1.8-2.2; Cu, 1; and that slight variations in the initial concentration of Bi and Sr favor the appearance of these phases. On the other hand, we observed that the nominal composition 2:2:1 is metastable and changes when heated for a long time. These observations are related to the results of some re-

cent studies^{26,38-40}. One of them²⁶ concludes that three phases coexist at the ideal 221 composition: a superconducting material with the approximate composition $\text{Bi}_{2.125}\text{Sr}_{1.875}\text{Cu}_{1.031}\text{O}_z$ and two oxides, $\text{Bi}_{17}\text{Sr}_{16}\text{Cu}_7\text{O}_y$ and $\text{Sr}_3\text{Cu}_5\text{O}_y$, the first of which with parameters $a = 5.425$, $b = 23.254$, $c = 24.427$ Å. The second study³⁸ points out that nominal 221 is actually a solid solution tolerating a range of Sr deficiency, i.e., $\text{Bi}_2\text{Sr}_{2-x}\text{CuO}_6$ ($x = 0.1-0.5$); that superconducting behaviour is observed for $x = 0.1-0.25$, the solid solution undergoing a metal-to-insulator transition for higher x values; and that the stable phase at the 221 composition is a semiconductor designed as the **collapsed** 221 phase. The results of the third study³⁹ confirm the existence of one oxide with Bi:Sr:Cu ratios of 2:2:1, and a solid-solution phase with $(2.2-x):(1.8+x):1$ ratios, for $x = 0-0.08$. Only this second phase is a superconductor at 9 K and $x = 0.08$. The 2:2:1 compound³⁹, the **collapsed**³⁸ 221 phase, and the oxide formulated²⁶ as $\text{Bi}_{17}\text{Sr}_{16}\text{Cu}_7\text{O}_y$ show the same X-ray diffraction pattern, that was indexed³⁹ with $a = 23.73(1)$, $b = 13.242(6)$, $c = 4.081(1)$ Å. By a combination of electron diffraction and single crystal and powder X-ray diffraction, the phase of composition 221 has been more recently found⁴⁰ to have a commensurate lattice with monoclinic symmetry, S.G. C2/m or Cm, $a = 24.473(2)$, $b = 5.4223(5)$, $c = 21.959(2)$ Å and $\beta = 105.40(1)^\circ$. In short, it appears that the superconducting oxide thought at the beginning as having the composition 221, is a solid solution with a range of Sr deficiency; and that stoichiometric 221 is not a superconductor. Hence, the structural data shown in Table II correspond to the Sr-deficient solid solution, and stoichiometric 221 is monoclinic, with the X-ray diffraction data³⁹ indicated. These two phases will be labelled here as A and K respectively.

At least five additional oxides with various Bi:Sr:Cu molar ratios have been described. Two of them, 2:7:2 and 4:9:1, are apparently stabilized by the presence of Li_2CO_3 , but do not form without it³⁹. Table III includes X-ray diffraction data for these oxides. The cubic oxide which appeared with some impurities from nominal molar ratios 2:4:1 showed⁴² the reflexions of a perovskite with 1:1 order at the B-cation sublattice. The authors found later that for Bi:Sr ratios 1:2 and 1:3 a very similar perovskite is formed without copper. This result led them to explore the Sr-rich region of the phase diagram $\text{Bi}_2\text{O}_3\text{-SrO}$. On the other hand, the authors

Table III. Unit-cell constants for oxides with various Bi:Sr:Cu ratios

Bi:Sr:Cu	Symmetry	a/Å	b/Å	c/Å	Refs.
2 3 2	0	4.888	5.396	24.804	26
4 8 5	0	5.389	24.050	34.035	26
4 8 5	0	5.373(2)	23.966(4)	33.907(6)	41
2 4 1	C	8.480(1)	-	-	42
2 7 2	0	8.769(2)	8.340(2)	7.983(3)	39
4 9 1	T	11.694(3)	-	9.466(4)	39
C: cubic		O: orthorhombic		T: tetragonal	

nary results of these experiments are included in this paper.

2. EXPERIMENTAL

Six polycrystalline samples of the compositions indicated in Table IV were prepared by solid-state reactions from mixtures of analytical grade Bi_2O_3 and SrCO_3 , which were ground and successively heated in air at 800, 900 and 950 °C in alumina crucibles. After each thermal treatment, which lasted five hours, the samples were weighed, reground and characterized by X-ray diffraction using a SIEMENS Kristalloflex D500.

Table IV. Phases identified in six polycrystalline samples of compositions $\text{Bi}_{2-2x}\text{Sr}_x\text{O}_{3-2x}$

No.	Bi : Sr	x	Phases
1	2.0 3	0.75	J+E(s)
2	3.0 5	0.77	J+E
3	4.0 7	0.78	E+J
4	1.0 2	0.80	E+J(s)
5	1.1 3	0.85	E+J(t)
6	1.0 3	0.86	E
J $\text{Bi}_2\text{Sr}_3\text{O}_6$		E $\text{BiSr}_3\text{O}_{5.5}$	
s small amounts		t traces	

of the crystals as grown was pulverized and characterized by X-ray diffraction. The d-spacings and relative intensities were measured as indicated elsewhere⁴³. The morphological study of the crystals was performed using a JEOL scanning microscope JSM 35-C. For high resolution electron microscopy and electron diffraction, a microscope JEOL JEM-2000 FX was employed. The resistivity measurements were made using a standard four-probe method.

3. RESULTS AND DISCUSSION

Table IV includes the phases identified in six polycrystalline samples of compositions $\text{Bi}_{2-2x}\text{Sr}_x\text{O}_{3-2x}$ ($0.75 \leq x \leq 0.86$): $\text{Bi}_2\text{Sr}_3\text{O}_6$ and $\text{BiSr}_3\text{O}_{5.5}$. The oxide with Bi:Sr = 2:3 molar ratio shows the following d spacings (Å) with the relative intensities in parentheses: 4.68(10); 4.38(8); 4.23(7); 4.01(10); 3.75(6); 3.14(90); 3.04(100); 2.18(50); 1.81(20); and 1.79(30). The oxygen content for $\text{BiSr}_3\text{O}_{5.5}$ has been adjusted assuming Bi (V), because the mass changes were followed by weighing before and after each operation and showed that almost the whole Bi (III) oxidized in the course of the thermal treatments. The X-ray powder diffraction pattern for $\text{BiSr}_3\text{O}_{5.5}$ shows

found that not too long treatments of mixtures with nominal composition 221 at 780–790 °C gave A and small amounts of $\text{Bi}_2\text{Sr}_2\text{O}_5$; that K was obtained with loss of mass after long treatments at 900 °C; and that K, when exposed to the air, becomes A_1 , a phase whose X-ray diffraction pattern looks very similar to that of A. These results led them to grow crystals of A, K and A_1 in different conditions. The preliminary

The crystals were grown from mixtures of 99.9 % Bi_2O_3 , $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and CuO at the molar ratios and conditions shown in Table V. Dense-alumina crucibles were used. Revolving crucibles (60 r.p.m.) with the direction of rotation changing every 10 seconds in a furnace QUASTAR 89 were employed for sample nos. 9–12. Except indicated otherwise (sample nos. 1, 9–11) the samples were preheated at 850 °C for 12 hours, quenched, ground, led to the temperature T (°C), maintained at this temperature for t hours as a melt, cooled to 750 °C at 2°C h^{-1} , and quenched. A portion

Table V. Phases identified in crystals grown from mixtures of various Bi:Sr:Cu molar ratios

No.	Bi: Sr: Cu	T/°C	t/h	Phases
1	2.0 2.0 1	890 ^a	6	A+A ₁ (s)
2	2.0 2.0 1	930	6	A
3	2.2 1.8 1	930	6	A ₁ +A(t)
4	1.8 2.0 1	1000	6	K
5	1.5 2.0 1	1000	6	K
6	1.8 2.2 1	930	6	K+G(s)
7	1.0 1.5 1	1000	6	A ₁ +G
8	0.7 1.0 1	1000	6	G
9*	2.0 2.0 1	940 ^{b,c}	1	K
10*	2.0 2.0 1	940 ^{d,c}	1	K
11*	2.0 2.0 1	940 ^c	1	A ₁
12*	2.0 2.0 1	940	1	A+K+A ₁

* revolving crucible ^a cooled to R.T.

^b crystallized at 15 °Ch⁻¹ ^c no pretreatment at 850°C

^d crystallized at 5 °Ch⁻¹ (s) small amounts (t) traces

A, Raveau phase; A₁, new phase; K, 221 oxide;

G, Bi₄Sr₈Cu₅O₁₉

the reflexions of a cubic perovskite, $a = 2a_0 = 8.493(7) \text{ \AA}$, with 1:1 order at the B-cations sublattice: Sr[Sr_{0.5}Bi_{0.5}]O_{2.75}. This oxide, which appears as not too crystalline, appears to substitute some Cu for Bi giving rise to materials like Sr[Sr_{0.5}Bi_{0.3}Cu_{0.2}]O_{2.45}, which was prepared from stoichiometric mixtures of Bi₂O₃, Sr(OH)₂·8H₂O and CuO heated as indicated for the basic compound. The unit-cell parameter of the Cu-containing material is slightly smaller, $a = 8.465(14) \text{ \AA}$. This could be expected from the different sizes⁴⁴ of both cations, 0.76 Å for Bi (V) and 0.73 Å for Cu (II), as well as from the smaller oxygen content of the Cu-containing oxide. This is the phase which appeared⁴² with some impurities from nominal 2:4:1. Apart from this, all the attempts to reproduce the X-ray diffraction pattern reported²⁶ for BiSr₃O₇ were unsuccessful.

All the experiments on crystal growth led to abundant masses of crystals in which the phases included in Table V (A, A₁, K and G) were identified. Three of these, A, K and G, are relatively well known: A, that was present in sample nos. 1, 2 and 12, is the Raveau phase with the unit-cell parameters included in Table II; K is monoclinic⁴⁰ 221, which appears as major product after crystallising sample nos. 4, 5, 6, 9 and 10; and G (samples 6-8) is orthorhombic^{26,41} Bi₄Sr₈Cu₅O₁₉. Crystals of A₁, a new phase closely related to A, are obtained from sample nos 3, 7, and 11. The relation between the X-ray diffraction patterns of both phases is shown in Fig. 1.

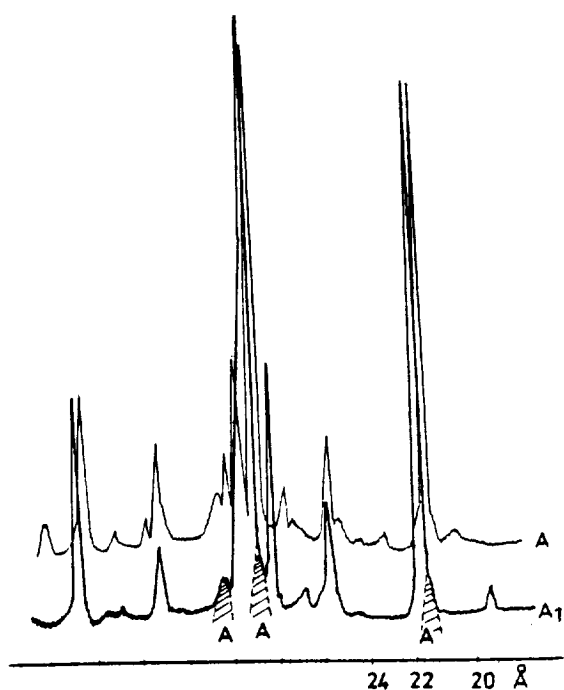


Fig. 1. Comparison of X-ray diffraction patterns of A₁ and A.

The morphologies of A and A₁ can only be distinguished by the way of their faces being developed. Crystals of A have planar faces, ordinarily well developed, some of them with edges up to 5 mm long, but forming irregular triangles as Fig. 2 shows. The A₁ phase shows a similar morphology and strong tendencies to be delaminated and to grow by steps. Consequently, voluminous crystals of A₁ cannot easily be grown. When static crucibles are employed, nominal mixtures with Bi:Sr ratio larger than 1 (sample no. 3) lead to A₁ as the major product, whereas stoichiometric 221 gives phase A (sample nos. 1 and 2). The

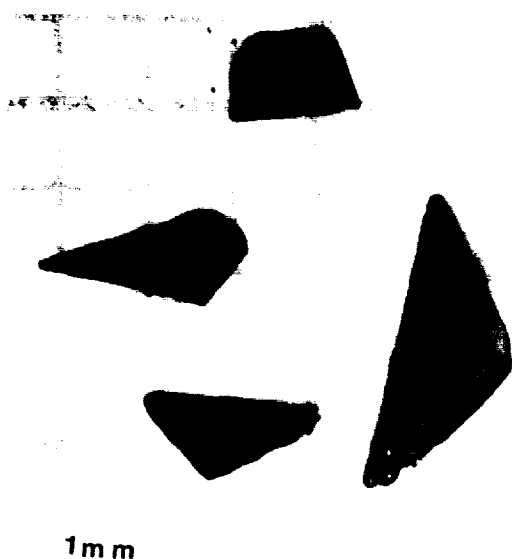


Fig. 2. Optical photomicrograph of the A phase.

10 leads to crystals of K, which is the phase with the smaller oxygen content. For a slower crystallization (sample no. 11), crystals of A_1 result. In the case of pretreated sample no. 12, with smaller oxygen content, the three phases appear at different heights of the crucible: A, at the bottom; A_1 , at the top; and K between A and A_1 . This suggests that A has incorporated all the oxygen of the melt at the expense of K, and that the external portion of K has oxidized in contact with air.

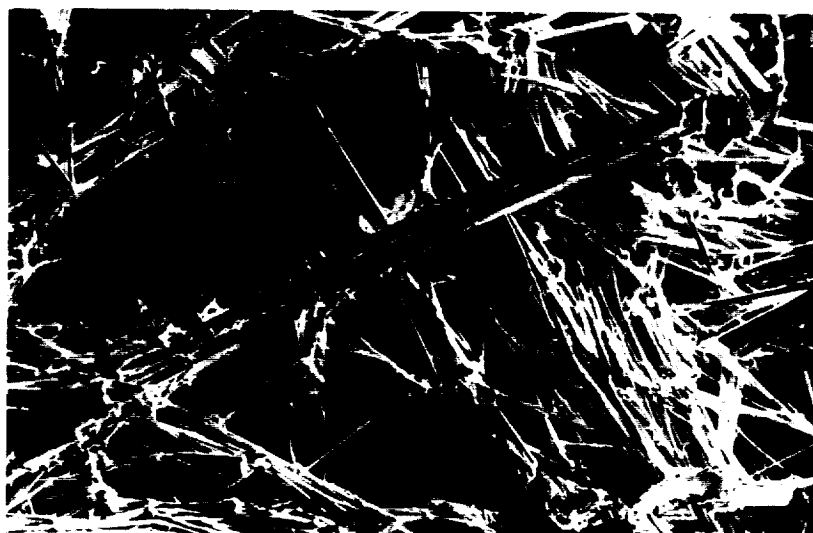


Fig. 3. SEM micrograph showing needle-like crystals of K up to 10 mm long.

Although K crystals obtained in static crucibles (sample nos. 4,5) are grown from mixtures with Bi:Sr ratios smaller than 1, and polycrystalline K is prepared from stoichiometric 221 after long thermal treatments at 900 °C in which some Bi can be lost, K crystals are grown in rotating crucibles at high crystallization rates from stoichiometric 221 mixtures (sample nos. 9-10). This suggests that this composition, 221, is also included in the stability region of the K phase.

In the selected-area diffraction pattern from a crystal of A_1 (sample no. 3), satellites along the b axis were observed. Although the (001) planes of A_1 ordinarily present a large number of deformations, modulations of 2.7 nm can be seen in Fig. 4,

that represents the high-resolution (HR) lattice image taken with the incidence [001]. The wavy aspect of the (001) planes can also be observed. The high-resolution lattice image of Fig. 5, taken with the incidence [100] from another crystal of A_1

presence of traces of A_1 in sample no. 1 can be related with the removal of some oxygen during the 15 days required for lowering from 750 °C to room temperature.

Crystals of phase K are obtained using static crucibles from nominal mixtures with Bi:Sr ratios smaller than 1 (sample nos. 4, 5). For still smaller Bi:Sr ratios, the oxide $\text{Bi}_4\text{Sr}_8\text{Cu}_5\text{O}_{19}$ is progressively stabilized (sample nos. 6-8). Crystals of the K oxide show an elongated development and form needle-shaped or fibrous masses including many crystals (Fig. 3).

The results obtained in the experiments with rotating crucibles (sample nos. 9-12) also suggest that the oxygen content increases in the order $K < A_1 < A$. The rapid crystallization of sample nos. 9 and

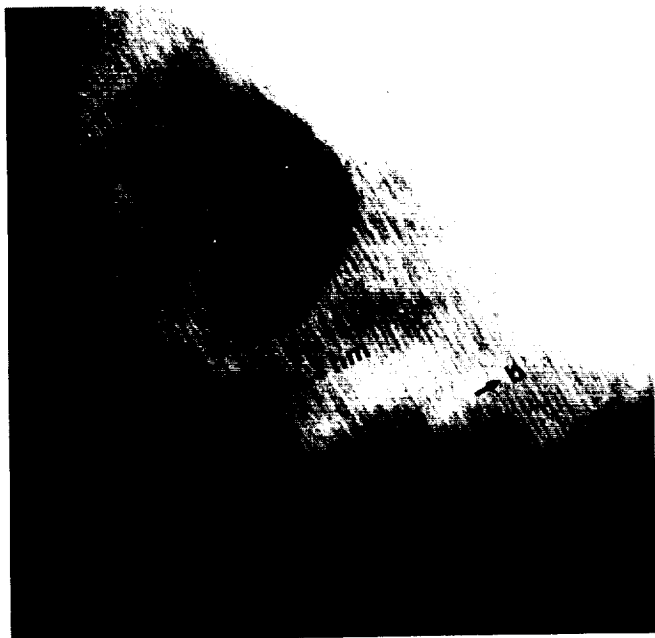


Fig. 4. High-resolution lattice image from A_1 with the incidence $[001]$.

(sample no. 3), contains modulations of 1.2 nm along the c axis. And Fig. 6, with the high-resolution lattice image of a different A_1 specimen (sample no. 1) taken with the incidence $[100]$, displays modulations of 11 and 9.5 nm along b and c axes respectively, the last of which comparable to those of $4 \times 2.4 = 9.6$ nm observed in the A phase by depth profile Auger analysis⁴⁵. In short, modulations along b and c axes observed in the A phase are also evident for A_1 .

Figs. 7 and 8 show the selected-area diffraction pattern taken with the incidence $[010]$ from a crystal of the K phase (sample no. 4) and the high-resolution lattice image of the same crystal showing modulations of 2.4 nm along the c axis.

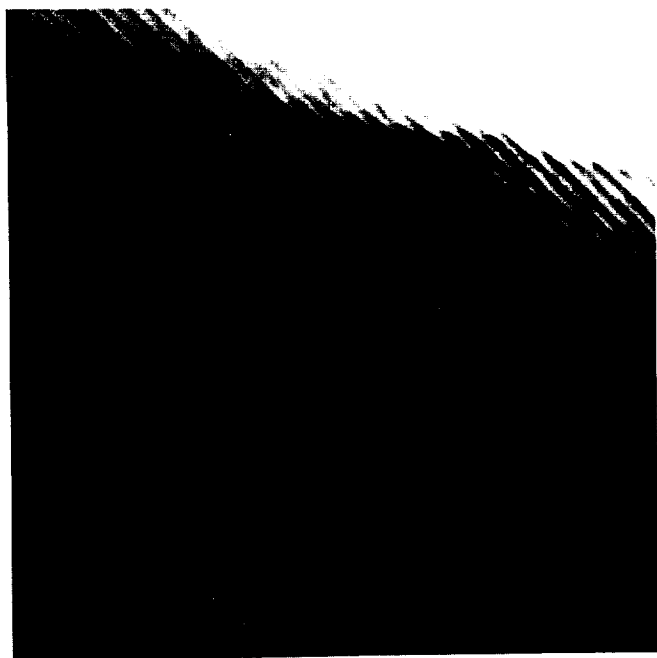


Fig. 5. HR lattice image of A_1 from sample no. 3, taken with the incidence $[100]$.



Fig. 6. HR lattice image of A_1 from sample no. 1, taken with the incidence $[100]$.

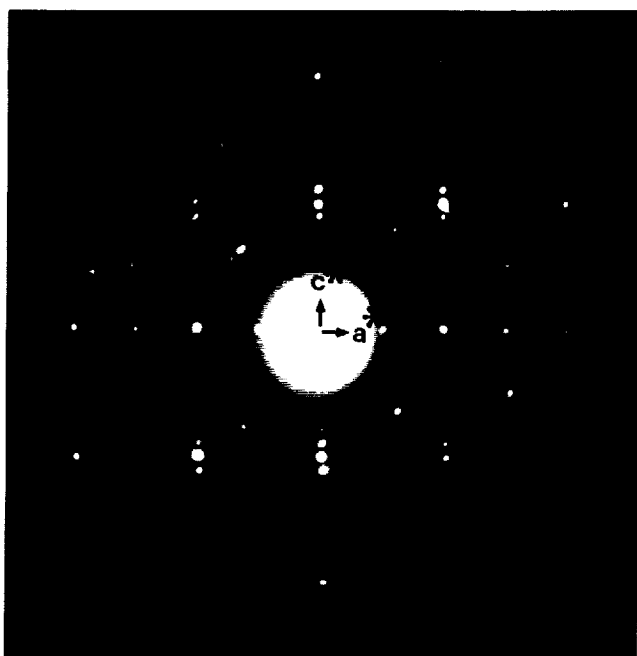


Fig. 7. Selected-area diffraction pattern from a crystal of the K phase.

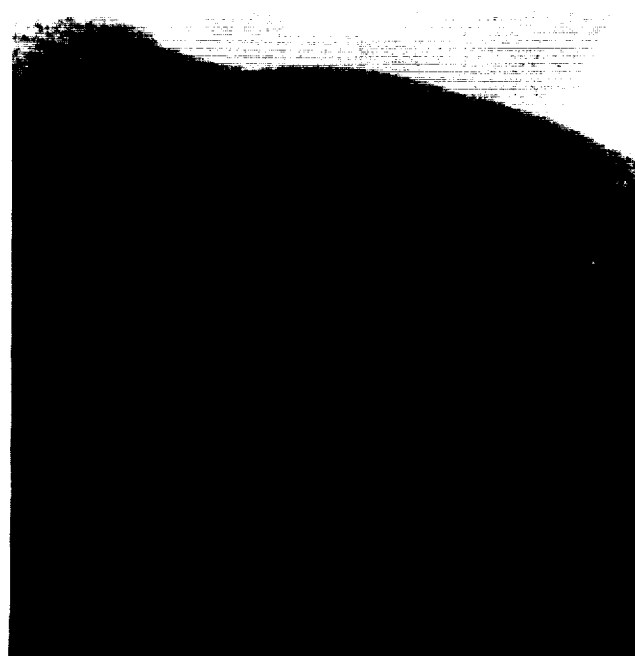


Fig. 8. HR lattice image of phase K taken with the incidence $[010]$.

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